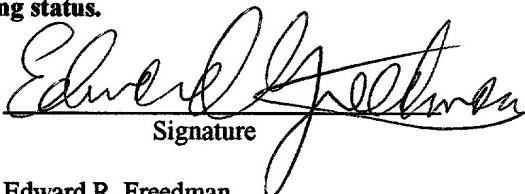
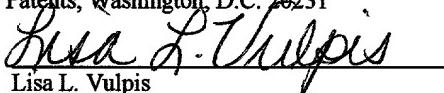


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|--|---|---|--|---|
| FORM PCT 1390<br>REV. 5/93   |   | U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE               |  | ATTORNEY'S DOCKET NO.<br><b>MÜHLEN ET AL.-1 (PCT)</b> |
| <b>TRANSMITTAL LETTER TO THE UNITED STATES<br/>DESIGNATED/ELECTED OFFICE (DO/EO/US)<br/>CONCERNING A FILING UNDER 35 U.S.C. 371</b>  |   | U.S. APPLICATION NO. (if known, see 37 CFR 1.5)<br><b>10 / 089012</b> |  |   |
| INTERNATIONAL APPLICATION NO.<br><b>PCT/EP00/09275</b>   | INTERNATIONAL FILING DATE<br><b>22 SEPTEMBER 2000</b> | PRIORITY DATE CLAIMED<br><b>24 SEPTEMBER 1999</b>                     |  |   |
| <b>TITLE OF INVENTION</b><br><b>METHOD FOR GASIFYING ORGANIC MATERIALS AND MIXTURES OF MATERIALS</b>   |   |   |  |   |
| <b>APPLICANT(S) FOR DO/EO/US</b><br><b>HEINZ-JÜRGEN MÜHLEN ET AL.</b>  |   |   |  |   |
| Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:  |   |   |  |   |
| <ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371 (f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l).</li> <li>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))             <ol style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau)</li> <li>b. <input type="checkbox"/> has been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li> <li>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).             <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> have been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has <b>NOT</b> expired.</li> <li>d. <input type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</li> <li>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</li> </ol> |   |   |  |   |
| <b>Items 11. to 16. below concern other document(s) or information included:</b>   |   |   |  |   |
| <ol style="list-style-type: none"> <li>11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.<br/><input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li>14. <input type="checkbox"/> A substitute specification.</li> <li>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>16. <input checked="" type="checkbox"/> Other items or information:<br/><br/>PCT/ISA/210 - Int'l. Search Report (English)<br/>2 sheets of formal drawings</li> </ol>   |   |   |  |   |
| Applicants Claim Priority under 35 U.S.C. §119 of German Application No. 199 45 771.9 filed September 24, 1999.<br>Applicants Claim Priority under 35 U.S.C. §120 of: PCT/EP00/09275 filed September 22, 2000.   |   |   |  |   |

|   |              |   |  |
|---|--------------|---|--|
| APPLICATION NO. (if known, see 37 CFR 1.4)  |              | INTERNATIONAL APPLICATION NO.<br>PCT/EP00/09275 | ATTORNEY'S DOCKET NO.<br>MÜHLEN ET AL. |
| <b>10 / 089012</b>  |              |   |  |
| <input checked="" type="checkbox"/> The following fees are submitted:<br><b>Basic National Fee (37 CFR 1.492(a)(1)-(5)):</b><br>Search Report has been prepared by the EPO or JPO..... \$890.00<br>International preliminary examination fee paid to USPTO (37 CFR 1.482)<br>..... \$690.00<br>Neither international preliminary examination fee paid (37 CFR 1.82) nor<br>international search fee (37 CFR 1.445(a)(2)) paid to USPTO..... \$1,040.00<br>International preliminary examination fee paid to USPTO (37 CFR 1.482)<br>and all claims satisfied provisions of PCT Article 33(2)-(4). .... \$100.00           |              | CALCULATIONS                                    | PTO USE ONLY                           |
|   |              | \$ 890.00                                       |  |
| <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>   |              |   |  |
| Surcharge of \$130.00 for furnishing the oath or declaration later than <u>20</u> <u>30</u> months from the earliest claimed priority date (37 CFR 1.492(e)).   |              |   |  |
| Claims  | Number Filed | Number Extra                                    | Rate                                   |
| Total Claims  | 20 - 20 =    | - 0 -   | X \$18.00                              |
| Independent Claims  | 1 - 3 =      | - 0 -   | X \$84.00                              |
| Multiple dependent claim(s) (if applicable)   |              | + \$280.00                                      |  |
| <b>TOTAL OF ABOVE CALCULATIONS =</b>  |              | \$ 890.00                                       |  |
| Reduction by 1/2 for Small Entity status.   |              | \$ 445.00                                       |  |
| <b>SUBTOTAL =</b>   |              | \$ 445.00                                       |  |
| Processing fee of \$130.00 for furnishing the English translation later than <u>20</u> <u>30</u> months from the earliest claimed priority date (37 CFR 1.492(f)).  |              | \$  |  |
| <b>TOTAL NATIONAL FEE =</b>   |              | \$ 445.00                                       |  |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +  |              | \$ 40.00  |  |
| <b>TOTAL FEES ENCLOSED =</b>  |              | \$ 485.00                                       |  |
|   |              | Amount to be:<br>refunded                       | \$                                     |
|   |              | charged   | \$                                     |
| <input checked="" type="checkbox"/> Applicant claims Small Entity status.<br>a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>485.00</u> to cover the above fees is enclosed.<br>b. <input type="checkbox"/> Please charge my Deposit Account No. 03-2468 in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.<br>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment, to Deposit Account No. 03-2468. A duplicate copy of this sheet is enclosed. |              |   |  |
| <b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b>  |              |   |  |
| SEND ALL CORRESPONDENCE TO:<br><b>COLLARD &amp; ROE, P.C.</b><br>1077 Northern Boulevard<br>Roslyn, New York 11576-1696<br>(516) 365-9802   |              |   |  |
| <br><b>Edward R. Freedman</b><br>Reg. No. 26,048  |              |   |  |
| <b>Express Mail No. EL 871 452 650 US</b><br><b>Date of Deposit March 25, 2002</b>  |              |   |  |
| I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C on the date indicated above, and is addressed to the Ass't. Commissioner for Patents, Washington, D.C. 20231  |              |   |  |
| <br>Lisa L. Vulpis  |              |   |  |

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANTS: HEINZ-JÜRGEN MÜHLEN ET AL. - 1 (PCT)

PCT NO.: PCT/EP00/09275

FILED: SEPTEMBER 22, 2000

TITLE: METHOD FOR GASIFYING ORGANIC MATERIALS AND MIXTURES OF MATERIALS

PRELIMINARY AMENDMENT

BOX PCT  
Ass't. Commissioner for Patents  
Washington, D.C. 20231

Dear Sir:

Preliminary to the initial Office Action, please amend the above-identified application as follows:

IN THE ABSTRACT:

Please add the attached Abstract of the Disclosure on a separate page.

IN THE SPECIFICATION:

On Page 1, above line 1, please insert the following paragraphs:

--CROSS REFERENCE TO RELATED APPLICATIONS

Applicants claim priority under 35 U.S.C. §119 of German Application No. 199 45 771.9 filed September 24, 1999.

Applicants also claim priority under 35 U.S.C. §120 of

PCT/EP00/09275 filed September 22, 2000. The international application under PCT article 21(2) was not published in English.--

**IN THE CLAIMS:**

Please amend claims 3-20 as follows:

3. (Amended) The method according to claim 1, characterized in that the heat-carrying medium consists of refractory substances such as sand, gravel, split, alumino-silicate, corundum, graywacke, quartzite, or cordierite.

4. (Amended) The method according to claim 1, characterized in that the heat-carrying medium consists of shaped bodies of metallic materials, and among such materials preferably of magnetic materials or non-metallic ceramic materials, and also sintered materials or iron ore pellets.

5. (Amended) The method according to claim 1, characterized in that the totality of the heat-carrying medium used consists at least partly of a material that is catalytically active in the second reaction zone.

6. (Amended) The method according to claim 1, characterized in that the separation of the heat-carrying medium from the solid, carbon-containing residue is carried out

mechanically upon exiting from the pyrolysis reactor via a single- or multi-stage screening stage.

7. (Amended) The method according to claim 1, characterized in that the separation of the heat-carrying medium from the solid, carbon-containing residue upon exiting from the pyrolysis reactor is carried out magnetically.

8. (Amended) The method according to claim 1, characterized in that the separation of the heat-carrying medium from the solid, carbon-containing residue is carried out upon exiting from the pyrolysis reactor pneumatically with the help of wind sifting, and that the sifting medium is preferably air, and in turn again preferably combustion air for the firing stage, or exhaust gas, in turn preferably again exhaust gas recycled from the firing stage.

9. (Amended) The method according to claim 1, characterized in that a portion of the pyrolysis gases or of the product gas is burnt in the firing stage for the carbon-containing residue, or in a separate firing stage, and the heat liberated in said stage is used in the pyrolysis and in the second reaction stage.

10. (Amended) The method according to claim 1, characterized in that a portion of the solid, carbon-containing

residue is recycled into the pyrolysis or the second reaction zone separately or together with the heat-carrying medium.

11. (Amended) The method according to claim 1, characterized in that at least one of the following media is conveyed discontinuously or in batches when exiting from the pyrolysis reactor: organic substance; heat-carrying medium; solid, carbon-containing residue; mixture of heat-carrying medium and solid, carbon-containing residue.

12. (Amended) The method according to claim 1, characterized in that the sensible heat of the product gas and the exhaust gas of the firing stage is at least partially used for generating the steam as the reactant, or for preheating the air for the firing stage.

13. (Amended) The method according to claim 1, characterized in that the sensible heat of the product gas and the exhaust gas of the firing stage is at least partially used for heating up the organic substance directly or indirectly.

14. (Amended) The method according to claim 1, characterized in that after passing through the heating-up zone, the heat-carrying medium is divided in a part passing through the second reaction zone, and a part directly used in the pyrolysis

reactor; and that the heat-carrying medium having passed through the second reaction zone, is passed on into the pyrolysis reactor, or is added to the remaining heat-carrying medium downstream of the pyrolysis reactor.

15. (Amended) The method according to claim 1, characterized in that the reactant, preferably steam, is admitted into the pyrolysis reactor at any desired point, preferably in a site located as closely as possible to the discharge of the mixture consisting of the heat-carrying medium and the solid, carbon-containing residue.

16. (Amended) The method according to claim 1, characterized in that a solid, liquid or gaseous fuel is at least partly used in the firing stage, such fuel neither being the material charged nor being formed at any point within the course of the process from said charged product or from any of its subsequent products.

17. (Amended) The method according to claim 1, characterized in that at least a partial stream of the solid, carbon-containing residue produced in the pyrolysis reactor is discharged and not burnt in the firing stage.

18. (Amended) The method according to claim 1,  
characterized in that the material charged is at least partially  
directly used as fuel in the firing stage.

19. (Amended) The method according to claim 1,  
characterized in that in addition to the heat-carrying medium, a  
highly basic, solid substance, preferably calcium oxide, calcium  
hydroxide or calcium carbonate is passed through the pyrolysis  
reactor, said substance being subsequently separated from the  
heat-carrying medium as well, and being passed either through the  
firing stage or directly discharged into the outside.

20. (Amended) The method according to claim 1,  
characterized in that the product gas is cooled and the  
condensation product formed in the cooling process is purified,  
if need be, and reused for generating the process steam, or added  
to the firing stage, or prior to the firing process, is added to  
the carbon-containing residue for the purpose of evaporation and  
combustion of the combustible components contained therein.

A marked-up version of prior pending claims 3-20 showing the  
changes made is attached as Exhibit A.

**REMARKS**

By this Preliminary Amendment, the application has been  
amended to conform with U.S. practice, the cross-reference to

related applications has been inserted on page 1, claims 3-20 have been amended to remove the multiple dependencies and an Abstract has been provided. No new matter has been introduced. Entry of this amendment is respectfully requested.

Respectfully submitted,  
HEINZ-JÜRGEN MÜHLEN ET AL.-1 (PCT)



Allison C. Collard, Reg. No. 22,532  
Edward R. Freedman, Reg. No. 26,048  
Attorneys for Applicants

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1077 Northern Boulevard  
Roslyn, New York 11576  
(516) 365-9802  
erf:jc  
Enclosure: Abstract  
Exhibit A

Express Mail No. EL 871 452 650 US  
Date of Deposit March 25, 2002

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. § 1.10, on the date indicated above, and is addressed to the Ass't. Commissioner for Patents, Washington, D.C. 20231

  
Lisa L. Vulpis

ABSTRACT OF THE DISCLOSURE

The aim of the invention is to provide a method for gasifying organic materials which is simple to carry out and requires minimal equipment and which produces an undiluted gas of high calorific value. The inventive method should eliminate the need to use fluid beds and heat exchangers with high temperatures on both sides, with the heat being transferred from the furnace to a heat-carrying medium in a particularly defined way. To this end, the feed material is divided into a volatile phase and a solid carbon-containing residue in the pyrolysis reactor by circulating a hot heat-carrying medium. After the reaction agent has been added, said volatile phase is converted into the product gas by further heating in the reaction area, also using the heat-carrying medium. The solid, carbon-containing residue is separated from the heat-carrying medium in the separating stage and burnt in the furnace. The heat-carrying medium is heated by the waste gases of the furnace in the heating area and then returned to the reformer and then the pyrolysis reactor.

**EXHIBIT A**

**Marked-up Version of Prior Pending  
Claims 3-20 Showing the Changes Made**

3. (Amended) The method according to claim 1 [any one of claims 1 and 2], characterized in that the heat-carrying medium consists of refractory substances such as sand, gravel, split, alumino-silicate, corundum, graywacke, quartzite, or cordierite.

4. (Amended) The method according to claim 1 [any one of claims 1 to 3], characterized in that the heat-carrying medium consists of shaped bodies of metallic materials, and among such materials preferably of magnetic materials or non-metallic ceramic materials, and also sintered materials or iron ore pellets.

5. (Amended) The method according to claim 1 [any one of claims 1 to 4], characterized in that the totality of the heat-carrying medium used consists at least partly of a material that is catalytically active in the second reaction zone.

6. (Amended) The method according to claim 1 [any one of claims 1 to 5], characterized in that the separation of the heat-carrying medium from the solid, carbon-containing residue is carried out mechanically upon exiting from the pyrolysis reactor via a single- or multi-stage screening stage.

7. (Amended) The method according to claim 1 [any one of claims 1 to 6], characterized in that the separation of the heat-carrying medium from the solid, carbon-containing residue upon exiting from the pyrolysis reactor is carried out magnetically.

8. (Amended) The method according to claim 1 [any one of claims 1 to 7], characterized in that the separation of the heat-

carrying medium from the solid, carbon-containing residue is carried out upon exiting from the pyrolysis reactor pneumatically with the help of wind sifting, and that the sifting medium is preferably air, and in turn again preferably combustion air for the firing stage, or exhaust gas, in turn preferably again exhaust gas recycled from the firing stage.

9. (Amended) The method according to claim 1 [any one of claims 1 to 8], characterized in that a portion of the pyrolysis gases or of the product gas is burnt in the firing stage for the carbon-containing residue, or in a separate firing stage, and the heat liberated in said stage is used in the pyrolysis and in the second reaction stage.

10. (Amended) The method according to claim 1 [any one of claims 1 to 9], characterized in that a portion of the solid, carbon-containing residue is recycled into the pyrolysis or the second reaction zone separately or together with the heat-carrying medium.

11. (Amended) The method according to claim 1 [any one of claims 1 to 10], characterized in that at least one of the following media is conveyed discontinuously or in batches when exiting from the pyrolysis reactor: organic substance; heat-carrying medium; solid, carbon-containing residue; mixture of heat-carrying medium and solid, carbon-containing residue.

12. (Amended) The method according to claim 1 [any one of claims 1 to 11], characterized in that the sensible heat of the product gas and the exhaust gas of the firing stage is at least partially used for generating the steam as the reactant, or for preheating the air for the firing stage.

13. (Amended) The method according to claim 1 [any one of claims 1 to 12], characterized in that the sensible heat of the

product gas and the exhaust gas of the firing stage is at least partially used for heating up the organic substance directly or indirectly.

14. (Amended) The method according to claim 1 [any one of claims 1 to 13], characterized in that after passing through the heating-up zone, the heat-carrying medium is divided in a part passing through the second reaction zone, and a part directly used in the pyrolysis reactor; and that the heat-carrying medium having passed through the second reaction zone, is passed on into the pyrolysis reactor, or is added to the remaining heat-carrying medium downstream of the pyrolysis reactor.

15. (Amended) The method according to claim 1 [any one of claims 1 to 14], characterized in that the reactant, preferably steam, is admitted into the pyrolysis reactor at any desired point, preferably in a site located as closely as possible to the discharge of the mixture consisting of the heat-carrying medium and the solid, carbon-containing residue.

16. (Amended) The method according to claim 1 [any one of claims 1 to 15], characterized in that a solid, liquid or gaseous fuel is at least partly used in the firing stage, such fuel neither being the material charged nor being formed at any point within the course of the process from said charged product or from any of its subsequent products.

17. (Amended) The method according to claim 1 [any one of claims 1 to 16], characterized in that at least a partial stream of the solid, carbon-containing residue produced in the pyrolysis reactor is discharged and not burnt in the firing stage.

18. (Amended) The method according to claim 1 [any one of claims 1 to 17], characterized in that the material charged is at least partially directly used as fuel in the firing stage.

19. (Amended) The method according to claim 1 [any one of claims 1 to 18], characterized in that in addition to the heat-carrying medium, a highly basic, solid substance, preferably calcium oxide, calcium hydroxide or calcium carbonate is passed through the pyrolysis reactor, said substance being subsequently separated from the heat-carrying medium as well, and being passed either through the firing stage or directly discharged into the outside.

20. (Amended) The method according to claim 1 [any one of claims 1 to 19], characterized in that the product gas is cooled and the condensation product formed in the cooling process is purified, if need be, and reused for generating the process steam, or added to the firing stage, or prior to the firing process, is added to the carbon-containing residue for the purpose of evaporation and combustion of the combustible components contained therein.

10/089012

JC13 Rec'd PCT/PTO 25 MAR 2002

2/pr/jr

METHOD FOR GASIFYING ORGANIC MATERIALS AND MIXTURES OF  
MATERIALS

The invention relates to a method for gasifying organic materials and mixtures of materials as defined in the introductory part of claim 1.

A process for gasifying organic substances and mixtures of substances is known from US-PS 4,568,362 [1], in which the organic substances are admitted into a pyrolysis reactor, in which these substances come into contact with a heat-carrying medium. Such contact leads to a high rate of pyrolysis and the substances are converted into pyrolysis products, i.e. pyrolysis gases containing condensable substances and solid, carbon-containing substances. The thermal energy required for the pyrolysis stage is generated by combusting the solid, carbon-containing residue. In a second reaction zone, the tar-containing pyrolysis gases are subjected to cracking reactions and reaction with steam in such a way that a gas product with a high calorific value is obtained.

In said process, both the pyrolysis and the combustion of the solid, carbon-containing residue take place in a fluidized bed. In the upper part of the fluidized-bed pyrolysis reactor, provision is made for a reaction zone for the tar-containing pyrolysis gases. The heat-carrying medium

is partially discharged together with the solid, carbon-containing residue via the reactor head of the fluidized-bed reactor, and the remaining part is discharged via a conduit arranged at the borderline of the upper fluidized bed, and supplied to the firing stage of the fluidized bed. There, the solid, carbon-containing residue is burnt, and the heat-carrying medium is heated up. The heated-up heat-carrying medium and the ash are jointly discharged with the exhaust gas from the fluidized-bed firing stage, separated in a gas/solids separator located above the fluidized-bed pyrolysis reactor, and supplied to the reaction zone of the pyrolysis reactor, from where they drop again into the fluidized bed of the pyrolysis reactor (= the heat-carrying medium circulation).

The operation of such fluidized beds, however, requires a substantial amount of expenditure, and it is hardly possible to exert any influence on the reactions of the pyrolysis gases occurring in the reaction zone. Furthermore, highly superheated steam has to be used in the reaction zone, which in turn requires the use of water that has been treated at substantial expenditure.

A process for gasifying organic substances and substance mixtures is known from DE-PS 197 55 693 [2]. In this process, the organic substances are brought into contact with a heat-carrying medium in a migrating-bed reactor,

which leads to rapid pyrolysis, with conversion of the organic substances into a carbon-containing, solid residue, on the one hand, and a pyrolysis gas that consists of condensable volatiles and gaseous components on the other.

The heat-carrying medium and the pyrolysis coke are subsequently supplied to a combustion stage, in which the carbon-containing residue is burnt, on the one hand, and the heat-carrying medium is heated up, on the other hand, before it is recycled into the pyrolysis stage.

After adding a reactant, which is steam, as a rule, the tar-containing pyrolysis gas is after-heated in a second reaction zone realized in the form of an indirect heat exchanger in such a way that a gas product with high calorific value is obtained. The heat exchanger takes place is indirectly heated by means of the combustion gases as the latter are being cooled. Following the firing process, the ash is separated from a partial stream of the mixture consisting of the heat-carrying medium and the ash of the solid, carbon-containing residue, and then cooled and discharged.

Said process, however, has a number of aspects that make a device for carrying out this process complicated in terms of the required expenditure and costly as well, and may also have an adverse influence on the operation and on the

availability as well. First of all, the heat-carrying medium is transported in the heated state from the combustion stage back into the pyrolysis stage, i.e. at a temperature that is by far above the pyrolysis temperature, which is specified to amount to from 550° to 650°C. This makes it imperative to employ special conveying means that require a particularly high amount of expenditure in terms of material and mechanically speaking. Furthermore, to the extent to which the heated heat-carrying medium is still mixed with ash, it has to be expected that the latter will escape and thus cause baking problems. Secondly, the indirect heat exchanger, owing of its operating conditions that include temperatures of from 500° to 1000°C on both sides, requires reducing conditions, on the one hand, and because of the highly corrosive components contained in both in the pyrolysis product and product gas and in the combustion exhaust gas as well, requires materials that require substantial expenditure, as well as an additional purification system that also may require much expenditure because of softening of the ash may possibly occur, on the other hand. The risk of ash baking to surfaces in the heat exchanger sets narrow limits for the operation and design of the firing stage as well. A further problem is encountered when steam is added to the pyrolysis gases: the steam is either superheated, which requires a great amount of expenditure, or the temperature is lowered, which may lead to condensation of tar and consequently to baking problems.

Finally, situations are conceivable in which it is not possible to assure a defined heat transfer into the heat-carrying medium as it is heating up again in the firing process, so it has to be feared that the pyrolysis coke and the heat-carrying medium are de-mixed in the firing stage, so that, for example in the case of a grate firing process, the pyrolysis coke is burnt off on the layer on top, whereas the heat-carrying medium may still be cooled by the current of grate air streaming in through the grate from the bottom.

The invention is based on the problem of providing a method that can be carried in a simple way for producing a high-quality and undiluted product gas with a high calorific value; with low expenditure for the equipment; and in which, furthermore, the use of fluidized beds or heat exchangers having high temperatures on both sides is avoided, and in which the heat is transferred from the firing stage into the heat-carrying medium in a particularly defined manner.

Said problem is solved by the combination of features specified in claim 1. In a manner similar to [2], the basic idea of dividing the method in three steps of the process that can be carried out in simple way, is pursued further as follows: rapid pyrolysis, recovery of the product gas from the pyrolysis gases after process steam has been added to the homogeneous gas phase reactions with feed of heat; and

generation of the heat required for the pyrolysis and initiation of the reactions of the gas phase by combusting pyrolysis coke of a solid, carbon-containing residue. However, a substantial expansion of the idea is represented by the fact that the heat of the firing stage is transferred into the heat-carrying medium in a defined and forcible manner, because if the pyrolysis coke and the heat-carrying medium are admitted into the firing stage in the form of a mixture, as it has been described in [2], it has to be expected that de-mixing of the heat-carrying medium and the pyrolysis coke will occur, for example on a combustion grate, so that the heat-carrying medium will not only be heated up inadequately in the course of the combustion process, but will even be cooled by the current of combustion air streaming in through the grate. A defined and enforced heat transfer is conceivable only in a rotating tubular furnace because the solids are intensively mixed there beyond the stoking effect of a grating. However, in conjunction with the present method, a rotating tubular furnace would represent a very costly firing system with poor admixture of the air, while a fluidized bed is disregarded for the reasons stated above.

Therefore, according to the invention, the mixture comprised of the pyrolysis coke and the heat-carrying medium is separated immediately after it has exited from the pyrolysis reactor; and the pyrolysis coke is then

transferred into the firing stage, whereas the heat-carrying medium is conveyed into a heating-up zone, through which it flows in the form of a fil of hot flue gas and where it is heated up in that way in a defined manner. Two aims are achieved by de-coupling the combustion of the pyrolysis coke in that way, on the one hand, and by heating up the heat-carrying medium on the other: the combustion of the pyrolysis coke can be completely adapted to the requirements of this fuel, on the one hand, i.e., it is basically made possible again to consider any type of firing. According to the method as defined by the invention, it is made possible, on the other hand, to shift the zone for heating up the heat-carrying medium to any desired location of a plant, so that the mechanical transport of the heat-carrying medium - which has been heated up to the maximum process temperature - is replaced by the comparatively simple transport of a hot exhaust gas coming from a firing stage; and the heat-carrying medium with the lowest process temperature, which is the temperature at the base after exiting from the pyrolysis reactor, is transported into the zone, where it is heated up again.

According to the invention, the pyrolysis of the organic substance is carried out in a reactor that permits converting the heat required for the heating up, and the drying steps and the pyrolysis to be carried out in a manner as effectively as possible, in conjunction with the greatest

possible simplicity in terms of equipment requirements, and a robust mode of operation. Consequently a migrating bed-type reactor or a rotating drum are considered for this task, as a rule. The pyrolysis temperature will then preferably be in a range of from 500° to 650°C.

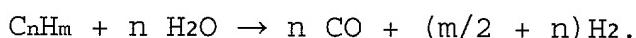
The type of separation method employed for separating the pyrolysis coke and the heat-carrying medium is dependent upon the quality of the heat-carrying medium, and may be carried out in different ways. A mechanical separation can be carried out, for example by means of a two-stage screening process. In such a screening process, the favorable effect is that the temperature of the media to be separated amounts to only about 500° to 600°C, so that it is possible to use materials that are currently available on the market. The separation by screening in two stages is considered if the heat-carrying medium consists of medium-sized particles within a narrow grain size spectrum. The heat-carrying medium is extracted in this screening process in the form of medium-sized material, whereas the pyrolysis coke is extracted in the form of coarse or fine material. As long as the two screening steps are carried out adequately close to each other, only rather minor amounts of pyrolysis coke will be getting into the heat-carrying medium, proportionately speaking, where this causes no disturbance, as a rule. Another possibility is the use of a heat-carrying medium with magnetic properties, for example such as steel

balls, which can be separated from the mixture with the help of a magnet. However, it has to be noted in this connection that magnetic separation of hot bulk materials is not as yet feasible with the components usually found in the market. Finally, the possibility of wind sifting is available provided the heat-carrying medium has adequate density. It is possible to use the combustion air as a sifting fluid medium; however, the medium is preferably a flue gas that has been recycled as a partial stream for safety reasons. It is recommended in such a case that the firing stage be located very close to the separation stage. The firing stage should, in this case, advantageously make use of the fluidization or dispersion of the fuel in the carrier gas, and should be, for example a cyclone firing process.

By separating the heat-carrying medium and the pyrolysis coke, the type of firing used is rendered almost insignificant. However, a few marginal conditions do in fact apply: On the one hand, at the given temperature of the reforming process, the flue has to be discharged at the end of the firing process with a temperature that takes into account the loss of heat incurred on the way to the heating-up zone; the concentration of the heat transfer to the heat-carrying medium within the heating-up zone, and the concentration of the heat-carrying medium when the heat is transferred into the second reaction zone in the course of the reforming process. If, for example, the temperature of

the reforming stage comes to 1000°C, the heat-carrying medium should have a hot temperature about 1050°C when it enters said zone. This can be achieved with hot flue gas having a temperature of 1075°C provided the heating-up zone is conceived accordingly. So as to cover the loss of heat occurring on the way from the firing stage to said heating-up zone, the flue gas has to be slightly hotter when it exits from the firing stage, i.e. it should have a temperature of, for example 1100°C. On the other hand, it is often necessary to maintain certain marginal conditions with respect to the mineral component of the pyrolysis coke. For example, melting or sintering of the ash does not have to be excluded, basically speaking; however, the ash, as a product, may require to be extracted in the dry state while avoiding any softening during such extraction, for example when chicken manure is gasified and the produced ash is to be used as a highly effective, valuable fertilizer. In such cases, it is possible to use, for example a stepped combustion process in an operation below the stoichiometric level of proportion, in which complete burning is achieved and the required temperature is thus generated only if secondary air is added. It has to be mentioned here also that in cases where the pyrolysis coke produced will not suffice for generating the process heat, product gas can be added to the firing stage.

The second reaction zone now included in the circulation of the heat-carrying medium represents the second important supplementation. The reforming process takes place in direct contact with the heat-carrying medium according to the known reactions with steam, for example according to:



Baking due to the possible formation of carbon black and other cracking processes is now made tolerable in this way because owing to the circulation of the heat-carrying medium, the heat-transferring surfaces are always regenerated time and again. The consequence of including the second reaction zone in the circulation of the heat-carrying medium is reflected by a substantial expansion of the circulation of the heat-carrying medium.

According to the invention, the method of the invention opens up at least two basic possibilities for controlling the circulation of the heat-carrying medium. With respect to the heat-carrying medium, it is possible to successively connect the second reaction zone and the pyrolysis reactor one after the other, in series or in parallel. The important advantage offered by the series connection lies in the simplicity of the equipment: the heating-up zone, the second reaction zone and the pyrolysis reactor are interconnected

among each other, so that the heat-carrying medium is moving through this arrangement, driven by force of gravity from the top downwards. Versus the arrangement described in [2], the pyrolysis stage has been changed to the extent that the pyrolysis no longer needs to be carried out with a very much greater amount of heat-carrying medium having, however, a distinctly lower temperature. If, for example, the heat-carrying medium enters the second reaction zone for the reforming purpose with a temperature of around 1050°C, it will exit from said zone while still having temperature of only about 750°C. With the parallel connection, the pyrolysis stage is not changed vis-à-vis the arrangement described in [2]. However, a higher expenditure in terms of equipment has to be expected due to the fact the hot stream of heat-carrying medium has been divided, allocating it to the pyrolysis reactor and the second reaction zone, and is subsequently united again. The parallel connection, therefore, has to be given preference in cases in which it is advantageous if the charged material comes into contact with particularly hot heat-carrying medium.

Finally, the addition of process steam to the pyrolysis gases prior to the reforming step is carried out in the second reaction zone. This is addressed in the following as well. The process steam has to be admixed in an excess amount with respect to the homogeneous reactions occurring in the gas phase that have to be expected to occur, because

any possible formation of carbon black can be consequently suppressed only in this way. A basis for this consists in maintaining a defined steam concentration in the fresh product gas, specifically amounting to, for example 20% by volume or more. On the other hand, it has to be expected that controlling the addition of process steam quantitatively with a steam concentration serving as the measuring quantity will require a great deal of expenditure and will be costly. It is deemed to be better to adjust a fixed value that is controlled via a measurement of the quantity depending on the capacity, which possibly may be carried out in any case. One possibility for realizing the method as defined by the invention that needs to be mentioned in any case lies in the selection of the site where the process steam is mixed with the pyrolysis gas. This mixing process has to take place prior to the entry of the mixture into the second reaction zone of the reformer at the latest; however, said site may be shifted upstream to the pyrolysis reactor, and there to any desired location within the pyrolysis reactor situated up to its lower end. The lower end of the pyrolysis reactor is meant in this connection to be the site from where the mixture comprising the heat-carrying medium and the solid, carbon-containing residue exits. This does change the division of the heat realized between the pyrolysis and the reforming stages; however, flushing of the pyrolysis with steam, which is added within the vicinity of the site where the solids exit

from the pyrolysis reactor, offers advantages in the last analysis under a number of aspects: firstly, the temperature of the pyrolysis gas is not lowered in this way at any point on its way to the second reaction zone, so no condensation has to be expected to occur. Secondly, it is known from [3] that it is possible to increase the yield of volatile components in the pyrolysis of biomasses by rinsing with steam. This can be advantageous because an excessively high yield of solid pyrolysis product beyond the heat requirement of the method will reduce the yield of product gas and in connection therewith the degree of efficiency of the cold gas. Thirdly and finally, this constitutes a preventive measure for avoiding possible leakage of pyrolysis gas in the direction of the separation stage, where the heat-carrying medium and the pyrolysis gas are separated.

FIG. 1 shows a possible embodiment of the object of the invention. This embodiment relates to the arrangement of the series connection described in the foregoing, in which the heating-up zone, the second reaction zone (the reformer) and the pyrolysis reactor are successively connected one after the other from the top down. The charged material 101 is supplied to the pyrolysis reactor 104 via a conveyor system 102 and the gate 103. The conveyor system 102 is a conveyor screw, a belt conveyor or a similar system that may be heated, whereby the low-temperature heat 151 obtained by exploiting the off-heat of the exhaust gas and the product

gas (see farther below) can be advantageously used specifically for raising the overall degree of efficiency. If an open system is used, the vapors 152 are exhausted into the environment, or otherwise added either to the pyrolysis reactor 104 or the firing stage 105. Adding the vapors to the pyrolysis reactor 104 has the advantage that a lesser amount of process steam needs to be supplied. However, it is, technically speaking, simpler if the vapors are added to the firing stage 105, because the latter is operated under a low vacuum. The pyrolysis reactor 104 is preferably designed in the form of a cylindrical shaft reactor. In addition to the charged material, the heat-carrying medium coming from the second reaction zone (= the reformer) 107 is dropping into said reactor via the gate 106 as well. The latter may have any desired type of construction; however, it is advantageously realized in the form of a bucket wheel gate or cycled thrust gate and needs not to be gas-tight.

The path followed by the expelled volatile components downstream is now described in the following first. The volatile components exit from the pyrolysis reactor 104 in mixture with the added process steam 109 via a separate conduit 108 and travel in the direction of the second reaction zone 107. Travelling via the gate 106 , which thus omits the separate conduit 108, would be basically feasible as well, notably if the gate could be realized in a permeable form in such a way that it would be permeable to

gas at any time without any restrictions, whereas the heat-carrying medium is permitted to enter the pyrolysis reactor 104 only in metered amounts or within the framework of the gating process, because while the heat-carrying medium is permitted to enter the pyrolysis reactor 104 only in metered amounts, with the possibility for interrupting the feed entirely, the total amount of the pyrolysis gas, in addition to the admixed process steam 109, has to be permitted to escape without being obstructed in any way. By suitably designing the bottom of the second reaction zone (= the reformer) 107 accordingly, the stream of the volatile components coming from the pyrolysis stage will pass through the fill of heat-carrying medium present in the reformer over as long a distance as possible. The heat-carrying medium is moving from the top down countercurrently in relation to the gas mixture, which is reacted to product gas while being heated up, and which is cooled on its way. For supporting the conversion process, the catalyst 111 in the form of a fill, or preferably in the form of a honeycombed packing, may be present in the upper part of the reformer 107. It is important that the catalyst 111 is located at the top, hot end of the reformer 107, because the product gas being formed is still unpurified at this point and may consequently still contain a number of catalyst toxins such as, for example sulfur depending on the charged stock material 101. However, many catalysts such as, for example the ones based on nickel, may be rendered more

insensitive or may even be regenerated or ``burnt free'', which could be achieved in the reformer 107 in a very simple way, for example by adding from time to time small amounts of air, whereby, however, a loss of product quality would have to be accepted during the time periods in which air is added. The product gas stream 112 exits from the reformer 107 in the upward direction. At the same time, the highest temperature is present at that point throughout the entire distance over which the pyrolysis gas or the product gas is travelling, so that the sensible heat of the product gas stream 112 should be exploited in any case. This can be accomplished in an advantageous way within the off-heat vessel 113. At least a portion of the steam generated there can then be recycled again into the process in the form of the process steam 109. After exploiting the off-heat, the raw product gas enters the purification and conditioning stage 114. The mode of operation of the latter is adapted to the subsequent purpose of application intended for the product gas, and is known per se. The purification stage 114 comprises at the same time conditioning of the aqueous condensation product obtained there, as a rule, by cooling the product gas. The adjustment of the pressure in the pyrolysis reactor 104, which preferably is a low vacuum, as well as the transport of the product gas and its preliminary runnings are handled by the ventilator 115. The purified product gas stream 116 exits from the plant system downstream of the ventilator 115. The condensation product

stream 153, which possibly may be conditioned, if need be, can now be supplied to the off-heat vessel 113 as the feed water, or can be evaporated in the firing stage 105, so that it is basically possible to control the process overall in a manner free of waste water. The possibility for supplying the condensation product to the firing stage consists in that the condensation product is supplied to the separation stage 121, which is described farther below, and evaporated under cooling of the heat-carrying medium or the carbon-containing residue, and the vapors are supplied to the firing stage. If the sensible heat is to be used to a very high extent, and steam may possibly have to be supplied to external consumers (which includes external conditioning of the stock material charged, or possibly internal conditioning in the conveyor 102 as well), it is recommended that only the fresh water 154 alone is used as feed water, whereas the condensation product 153 is discarded or ``burnt'' as completely as possible.

The path followed by the heat-carrying medium and the pyrolysis gas is described further as follows: The mixture comprising the heat-carrying medium and the pyrolysis gas passes through the gate and conveyor unit 120 and enters the separation stage 121. The mode of operation of the latter, which is working mechanically by means of screening or sifting, or magnetically, has already been described above. The separated pyrolysis coke stream 122 is subsequently

received in the firing stage 105, and received there immediately in the best way. It is burnt there with the combustion air 155 to a hot exhaust gas, which is conveyed via the hot gas conduit 123 to the heating-up zone 117 (= the preheater) for heating up the heat-carrying medium. The possibilities for decoupling the temperature in the burnt material and the temperature of the flue gas from each other via the excess air or the recycled flue gas, as well as for a stepped combustion process are known, so that de-ashing can be carried out in a dry way in spite of the required flue gas temperature. These possibilities are therefore not addressed here at greater length. What remains to be addressed is the ash/slag stream 156, which exits from the firing stage to the outside and is cooled on its way, if necessary.

The heat-carrying medium is directed transported to the preheater 117 by means of the conveyor system 124. The conveyor system has to be designed in such a way that it is capable of transporting hot material in a careful way, mechanically speaking, while minimizing the loss of heat. The use of a bucket conveyor system, a tubular chain conveyor or a bucket elevator system is primarily thought of in this connection.

In the present embodiment as defined by the invention, the preheater 117 is arranged directly on top of the

reformer 107 and separated from the latter on the gas side by the gate 118. Said gate has to be gas-tight the highest possible degree, so that no mixing of flue gas and product gas will occur. No special requirements have to be satisfied with respect to the type of construction of the gate 118 used. Analogous to the reformer 107, the exhaust gas flows through the preheater from the bottom to the top countercurrently in relation to the heat-carrying medium. The latter enters the preheater 17 at the top at the base temperature of the process of about 500°C. Said base temperature follows from the final pyrolysis temperature less a temperature reduction due to heat losses. If the preheater 117 is provided with an adequately large size (the same applies to the reformer 107), the conveyor system 124 as well as the gate elements 118 and 106 are capable of operating almost discontinuously in any desired way.

The off-gas exits from the preheater 117 at a temperature slightly above the temperature prevailing at the base. As a rule, the amount of off-gas is distinctly larger than the amount of the product gas. The use of the off-heat of the exhaust gas after it exits from the preheater is consequently urgently recommended in the present case. This is preferably accomplished by preheating the combustion air in the air preheater (LUVO) 125, because the recovered heat can be used again in this way in the following combustion stage, and is available above the base temperature of

approximately 500°C. This type of shifting of the heat cannot be produced in the way of steam generation or only so with a disproportionately high amount of expenditure. The purification stage 126 and the suction blower 127, which have to be configured depending on the material being processed and in light of the applicable restrictive emission regulations, their modes of operation being known per se, are arranged downstream of the air preheater (LUVO) 125. The purified exhaust gas 157 is released into the environment, as a rule, whereby a partial stream 158 can be recycled into the firing stage 105 for the purpose of superior temperature control.

FIG. 2 shows in a simplified manner the core of the plant in terms of process engineering on the side of the heat-carrying medium in the parallel arrangement of the second reaction zone (= the reformer) and the pyrolysis reactor. The path followed by the charged material 201 through the pyrolysis reactor 202 and the separation stage 203 to the firing stage 204 (combustion air 251) remains essentially the same. However, in the present embodiment, the reformer 205 is located next to the pyrolysis reactor at about the same level, and the preheater 206 representing the heating-up zone is installed above the pyrolysis reactor 202 and the reformer 205. The maximally heated heat-carrying medium is conveyed in parallel into the reformer 205 and the pyrolysis reactor 202 from the preheater 206 and by way of the now-two

indicated discharging funnels and the metering gates 207 and 208, which can be operated independently of one another. The heat-carrying medium exiting from the reformer 205 is not processed via the separation stage 203. However, the heat-carrying medium that has passed through the pyrolysis reactor 202 and has been separated from the pyrolysis coke in the separation stage 203, and the heat-carrying medium that has passed through the reformer 205, each are jointly transported in the conveying device 209 into the preheater 206. However, as far as the raw product gas stream 210 and the exhaust gas stream 211 downstream of the preheater 206 are concerned, everything remains the same as in the series connection of the arrangement shown in FIG. 1, so that the representation of the parallel circuit can be discontinued at this point.

FIG. 3 shows, in a highly simplified manner, a special case of application of the method as defined by the invention with the help of the example of the series circuit shown in FIG. 1, whereby said case of application is functioning in the parallel circuit shown in FIG. 2 in a corresponding manner. In the present embodiment, the charged stock material 300 enters the pyrolysis reactor 301 in the usual way and passes through the latter while the pyrolysis coke is being formed. However, in the present case, the latter is separated from the heat-carrying medium in the separation stage 302, and then extracted from the process as

the usable coke 304 via the cooling and conditioning stage 303, and subsequently used further in any desired way. In the present case, the stage 303 may be a changing vessel put under vacuum, but also a device used for dry quenching of the coke. The firing product 305 is now burnt with at least one of the fuels for the purpose of heating up the heat-carrying medium, using a foreign fuel 306 or a partial stream 307 of the product gas, or a partial stream 308 of the pyrolysis coke. However, the fuel 306 may be a partial stream of the charged material 300 as well, provided the latter can be fired. This is important especially in the start-up phase of a plant operating according to the method as defined by the invention. A great number of gaseous, liquid or solid fuels are considered otherwise. If, for example, the product gas is to be used as a reducing agent in a smelting process, stack gas or some other weak gas can be employed as the fuel 306. In the cases described in FIG. 3, the site of the firing 305 is no longer necessarily located within the direct proximity of the separation stage 302, but can be shifted to about the direct vicinity of the heating-up zone 309. This will not affect either the reformer 310 or the quality of the product gas 311 and the further treatment of the exhaust gas 312. FIG. 3 shows, furthermore, the conveyor system for the heat-carrying medium 313; the charging gate for feeding the stock material 320; the gate located between the reformer and the pyrolysis reactor 321; the extraction gate for the extraction from the

pyrolysis reactor 322; the gate located between the heating-up zone and the reformer 323; the combustion air stream 351; as well as the process steam stream 352.

Example of implementation of the method:

200 kg/h (afro) timber, i.e. 286 kg/h air-dried timber with a 30% moisture content is gasified in the device according to FIG. 1. The timber is assumed to contain 2% ash (anhydrous) and otherwise substantially 50% carbon, 6% hydrogen, 42% oxygen, and 1.9% nitrogen, calculated free of water and ash. The lower calorific value is assumed to amount to 18.0 MJ/kg in the anhydrous state. The thermal gasification capacity is assumed to consequently amount to 1,000 kW. The pyrolysis is assumed to be carried out at 550°C and the reforming step to be carried out with steam at 950°C. The atmospheric pressure is the operating pressure.

Steel balls with a grain size of about 10 mm are employed as the heat-carrying medium. The heat-carrying medium is first heated from 500°C to 950°C. Because of the heat capacity of 251 kW required for the pyrolysis and the reforming stages, as well as for covering heat losses, the circulating amount of the heat-carrying medium amounts to 4,300 kg/h, and thus comes to 21.5 times the amount of timber charged. The pyrolysis reactor is a brick-lined shaft with a clear cylindrical height of 1.3 m and an inside

diameter of 0.9 m, so that the pyrolyzing migrating bed is safely provided with a dwelling time of 0.5 hour available to it. In the course of the pyrolyzing process, the timber is reacted in such a way that 20 percent by mass of the dry substance of the timber is left over as pyrolysis coke, thus 42 kg/h. Said pyrolysis coke has an ash component of 9.5% and contains 92.2% carbon, 2.6% hydrogen, and 5.2% oxygen on an anhydrous and ash-free basis. The calorific value amounts to 29.1 MJ/kg. The reforming process takes place at 950°C in a fill of the heat-carrying medium having a clear cylindrical height of 0.9 m and a clear diameter of 0.7 m, so that a gas dwelling time of 0.5 second is safely maintained. The following product gas is obtained in this way:

|                            |   |                        |
|----------------------------|---|------------------------|
| Calorific value            | : | 9.10 MJ/kg, dry        |
| Hydrogen                   | : | 59.7% by vol., dry     |
| Carbon monoxide            | : | 17.0 % by vol., dry    |
| Methane                    | : | 1.4% by vol, dry       |
| Carbon dioxide             | : | 21.9% by vol., dry     |
| Steam                      | : | 24.8% by vol.          |
| Quantity                   | : | 402 Nm <sup>3</sup> /h |
| Chemical enthalpy current: |   | 765 kW.                |

The enthalpy current of the pyrolysis coke in the firing stage amounts to 341 kW. The heat for the reforming stage, the pyrolysis, the waste water evaporation from the product

gas cooling stage, and for covering the heat losses is generated in this way, and the combustion air required in the firing stage is heated to 350°C. The degree of efficiency of the firing process amounts to 80.1%; the loss of exhaust gas consequently comes to 68 kW. The sensible heat of the product gas amounts to 168 kW, with which about 145 kg/h of a saturated steam with low pressure can be generated, whereof 50 kg/h is required as process steam in the reforming stage, while the remainder can be used in some other way.

[1] US-PS 4,568,362

[2] DE-PS 197 55 693

[3] M. Steseng, A. Jensen, K. Dam-Johansen, M. Gronil:  
Experimental Investigation and Kinetic Modelling of Biomass Pyrolysis; Proc. 2<sup>nd</sup> Olle Lindström Symposium, Stockholm  
June 8 to 11, 1999, pp 97-104.

### List of Reference Numerals

- 101 Charged material
- 102 Conveyor system for charged material
- 103 Gate
- 104 Pyrolysis reactor
- 105 Firing stage
- 106 Gate
- 107 Second reaction zone (reformer)
- 108 Separate conduit for volatile components
- 109 Admitted process steam
- 110 Heat-carrying medium
- 111 Catalyst
- 112 Product gas stream
- 113 Of-heat vessel
- 114 Purifying and conditioning stage
- 115 Ventilator
- 116 Purified product gas stream
- 117 Heating-up zone (= preheater)
- 118 Gate
- 120 Gate and conveyor unit
- 121 Separation stage
- 122 Pyrolysis coke stream
- 123 Hot gas conduit
- 124 Conveying element
- 125 Air preheater (LUVO)
- 126 Purification stage
- 127 Suction exhaust blower

151 Low-temperature heat  
152 Vapors  
153 Condensation product stream  
154 Fresh water  
155 Combustion air  
156 Ash/slag stream  
157 Purified exhaust gas  
158 Partial stream of purified gas

201 Charge material  
202 Pyrolysis reactor  
203 Separation stage  
204 Firing  
205 Reformer  
206 Preheater  
207 Metering gate  
208 Metering gate  
209 Conveying element  
210 Raw product gas stream  
211 Exhaust gas stream  
251 Combustion air

300 Charged material  
301 Pyrolysis reactor  
302 Separation stage  
303 Cooling and conditioning stage  
304 Usable coke

- 305 Firing
- 306 Foreign fuel
- 307 Product gas
- 308 Partial stream of pyrolysis coke
- 309 Heating-up zone (= preheater)
- 310 Reformer
- 311 Product gas
- 312 Exhaust gas
- 313 Conveyor system for heat-carrying medium
- 320 Charging gate for feeding the charged material
- 321 Gate between reformer and pyrolysis reactor
- 322 Extraction gate from extraction from pyrolysis reactor
- 323 Gate between heating-up zone and reformer
- 351 Combustion air stream
- 352 Process steam stream.

## Claims

1. A method for gasifying organic substances and substance mixtures, in connection with which the organic substances are split in a pyrolysis reactor through contact with a hot heat-carrying medium into a carbon-containing residue and pyrolysis gases; and the solid, carbon-containing residue is supplied to a firing stage and burnt there, whereby at least proportions of the liberated heat are used for heating up the heat-carrying medium; and the pyrolysis gases, after possibly adding a reactant such as steam in a second reaction zone, and with the use of at least a portion of the heat liberated in the firing stage, are after-heated through indirect heat exchange in such a way that a product with a high calorific value is obtained, characterized in that

- (a) the heat-carrying medium, upon exiting from the pyrolysis reactor, is separated from the solid, carbon-containing residue in a separation stage and supplied to a heating-up zone;
- (b) the solid, carbon-containing residue is burnt in a firing stage;
- (c) the hot exhaust gases of the firing stage are passed in the heating-up zone through a fill of the heat-carrying medium, whereby they transfer a large

- part of their sensible heat to the heat-carrying medium;
- (d) the heated-up heat-carrying medium is extracted from the heating-up zone into the second reaction zone designed in the form of a migrating bed reactor, where the mixture comprised of pyrolysis gases and reactant is heated up and converted into the product gas; and
- (e) the heat-carrying medium is recycled into the pyrolysis reactor after passing through the second reaction zone.

2. The method according to claim 1, characterized in that of the reaction of pyrolysis gases with the steam is carried out in the presence of a catalyst.

3. The method according to any one of claims 1 and 2, characterized in that the heat-carrying medium consists of refractory substances such as sand, gravel, split, aluminosilicate, corundum, graywacke, quartzite, or cordierite.

4. The method according to any one of claims 1 to 3, characterized in that the heat-carrying medium consists of shaped bodies of metallic materials, and among such materials preferably of magnetic materials or non-metallic ceramic materials, and also sintered materials or iron ore pellets.

5. The method according to any one of claims 1 to 4, characterized in that the totality of the heat-carrying medium used consists at least partly of a material that is catalytically active in the second reaction zone.

6. The method according to any one of claims 1 to 5, characterized in that the separation of the heat-carrying medium from the solid, carbon-containing residue is carried out mechanically upon exiting from the pyrolysis reactor via a single- or multi-stage screening stage.

7. The method according to any one of claims 1 to 6, characterized in that the separation of the heat-carrying medium from the solid, carbon-containing residue upon exiting from the pyrolysis reactor is carried out magnetically.

8. The method according to any one of claims 1 to 7, characterized in that the separation of the heat-carrying medium from the solid, carbon-containing residue is carried out upon exiting from the pyrolysis reactor pneumatically with the help of wind sifting, and that the sifting medium is preferably air, and in turn again preferably combustion air for the firing stage, or exhaust gas, in turn preferably again exhaust gas recycled from the firing stage.

9. The method according to any one of claims 1 to 8, characterized in that a portion of the pyrolysis gases or of the product gas is burnt in the firing stage for the carbon-containing residue, or in a separate firing stage, and the heat liberated in said stage is used in the pyrolysis and in the second reaction stage.

10. The method according to any one of claims 1 to 9, characterized in that a portion of the solid, carbon-containing residue is recycled into the pyrolysis or the second reaction zone separately or together with the heat-carrying medium.

11. The method according to any one of claims 1 to 10, characterized in that at least one of the following media is conveyed discontinuously or in batches when exiting from the pyrolysis reactor: organic substance; heat-carrying medium; solid, carbon-containing residue; mixture of heat-carrying medium and solid, carbon-containing residue.

12. The method according to any one of claims 1 to 11, characterized in that the sensible heat of the product gas and the exhaust gas of the firing stage is at least partially used for generating the steam as the reactant, or for preheating the air for the firing stage.

13. The method according to any one of claims 1 to 12, characterized in that the sensible heat of the product gas and the exhaust gas of the firing stage is at least partially used for heating up the organic substance directly or indirectly.

14. The method according to any one of claims 1 to 13, characterized in that after passing through the heating-up zone, the heat-carrying medium is divided in a part passing through the second reaction zone, and a part directly used in the pyrolysis reactor; and that the heat-carrying medium having passed through the second reaction zone, is passed on into the pyrolysis reactor, or is added to the remaining heat-carrying medium downstream of the pyrolysis reactor.

15. The method according to any one of claims 1 to 14, characterized in that the reactant, preferably steam, is admitted into the pyrolysis reactor at any desired point, preferably in a site located as closely as possible to the discharge of the mixture consisting of the heat-carrying medium and the solid, carbon-containing residue.

16. The method according to any one of claims 1 to 15, characterized in that a solid, liquid or gaseous fuel is at least partly used in the firing stage, such fuel neither being the material charged nor being formed at any point

within the course of the process from said charged product or from any of its subsequent products.

17. The method according to any one of claims 1 to 16, characterized in that at least a partial stream of the solid, carbon-containing residue produced in the pyrolysis reactor is discharged and not burnt in the firing stage.

18. The method according to any one of claims 1 to 17, characterized in that the material charged is at least partially directly used as fuel in the firing stage.

19. The method according to any one of claims 1 to 18, characterized in that in addition to the heat-carrying medium, a highly basic, solid substance, preferably calcium oxide, calcium hydroxide or calcium carbonate is passed through the pyrolysis reactor, said substance being subsequently separated from the heat-carrying medium as well, and being passed either through the firing stage or directly discharged into the outside.

20. The method according to any one of claims 1 to 19, characterized in that the product gas is cooled and the condensation product formed in the cooling process is purified, if need be, and reused for generating the process steam, or added to the firing stage, or prior to the firing process, is added to the carbon-containing residue for the

purpose of evaporation and combustion of the combustible components contained therein.

R:\Ingrid\email\Muhlen et al PCT transl.

(12) NACH DEM VERTRÄGE ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
PATENTWAHLRECHTS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

**(19) Weltorganisation für geistiges Eigentum  
Internationales Büro**



(43) Internationales Veröffentlichungsdatum  
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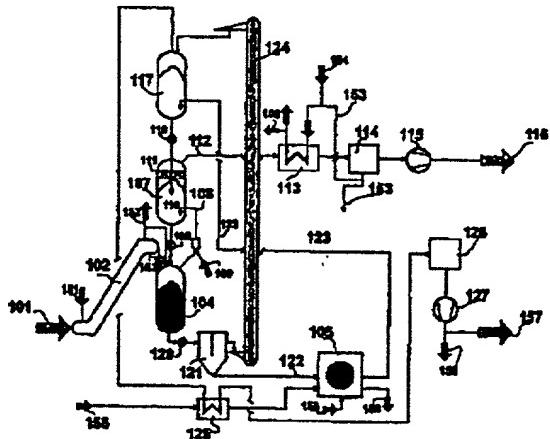
(10) Internationale Veröffentlichungsnummer  
**WO 01/21730 A1**

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| (51) Internationale Patentklassifikation:<br>49/16                             | C10B 53/02.    | (71) Anmelder ( <i>für alle Bestimmungsstaaten mit Ausnahme von US</i> ): DR. MÜHLEN GMBH & CO. KG [DE/DE]; Konrad-Adenauer-Strasse 9-13, 45699 Herten (DE).                                |
| (21) Internationales Aktenzeichen:   | PCT/EP00/09275 | (72) Erfinder; und  |
| (22) Internationales Anmeldedatum:<br>22. September 2000 (22.09.2000)          |                | (75) Erfinder/Anmelder ( <i>nur für US</i> ): MÜHLEN, Helaz-Jürgen [DE/DE]; Am Borggarten 12, 48167 Münster (DE). SCHMID, Christoph [DE/DE]; Talsperrenstrasse 21, 51702 Bergneustadt (DE). |
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| (26) Veröffentlichungssprache:   | Deutsch        | (81) Bestimmungstaaten ( <i>national</i> ): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU,   |
| (30) Angaben zur Priorität:<br>199 45 771.9 24. September 1999 (24.09.1999) DE |                |   |

[Fortsetzung auf der nächsten Seite]

(54) Title: METHOD FOR GASIFYING ORGANIC MATERIALS AND MIXTURES OF MATERIALS

**(54) Bezeichnung: VERFAHREN ZUR VERGASUNG VON ORGANISCHEN STOFFEN UND STOFFGEMISCHEN**



(57) Abstract: The aim of the invention is to provide a method for gasifying organic materials which is simple to carry out and requires minimal equipment and which produces an undiluted gas of high calorific value. The inventive method should eliminate the need to use fluid beds and heat exchangers with high temperatures on both sides, with the heat being transferred from the furnace to a heat-carrying medium in a particularly defined way. To this end, the feed material (101) is divided into a volatile phase and a solid carbon-containing residue in the pyrolysis reactor (104) by circulating a hot heat-carrying medium. After the reaction agent (109) has been added, said volatile phase is converted into the product gas by further heating in the reaction area (reformer) (107), also using the heat-carrying medium. The solid, carbon-containing residue is separated from the heat-carrying medium in the separating stage (121) and burnt in the furnace (105). The heat-carrying medium is heated by the waste gases of the furnace (105) in the heating area (117) and then returned to the reformer (107) and then the pyrolysis reactor (104).

(57) Zusammenfassung: Die Aufgabe, ein einfach durchzuführendes Verfahren zur Vergasung von organischen Stoffen mit geringem apparativen Aufwand zur Verfügung zu stellen, mit dem ein unverdünntes, beizwertsiches Produktgas hergestellt wird, und bei dem auf den Einsatz von Wirbelschichten und Wärmetauschern mit beidseitig hohen Temperaturen verzichtet, und die Wärme in besondere definiert Weise von der Feuerung an ein

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**Fig. 1**

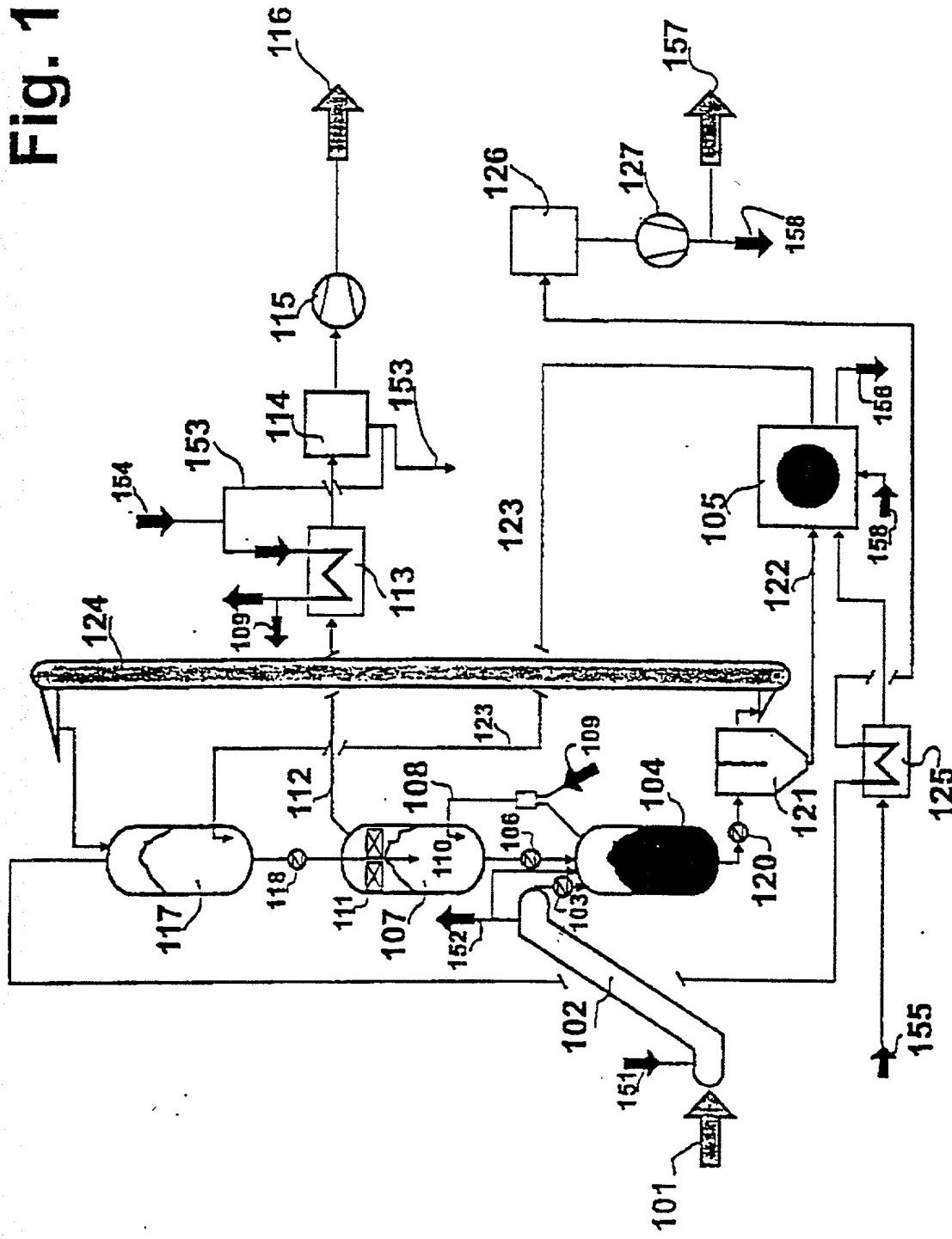


Fig. 2

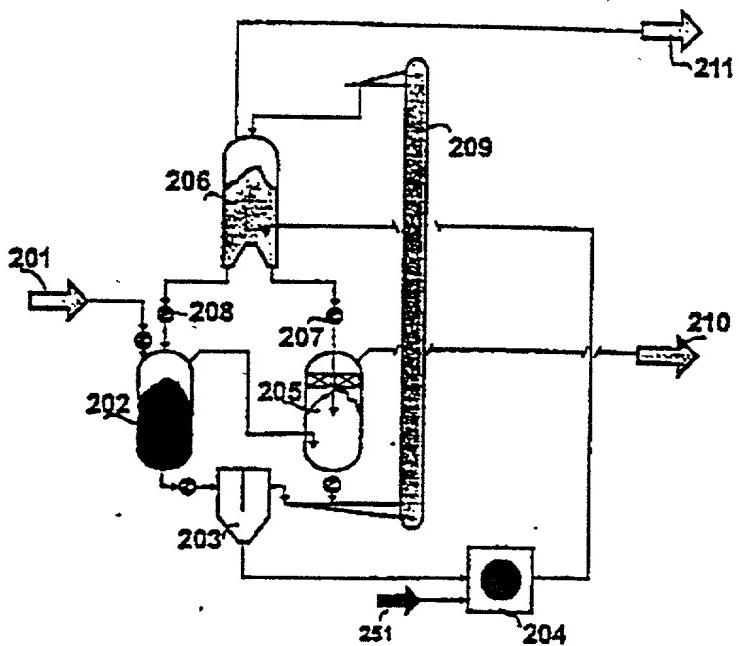
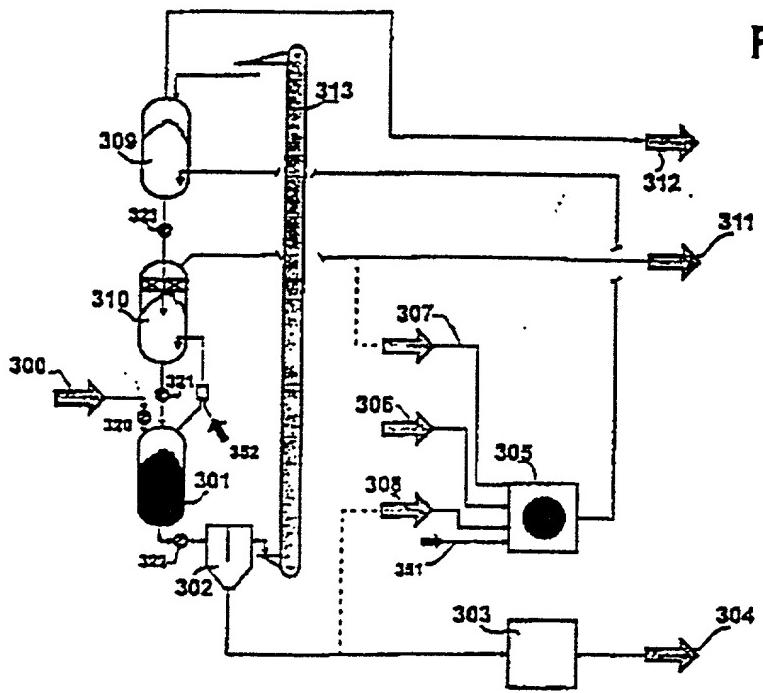


Fig. 3



DHDHoozo

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**  
 (Includes Reference to PCT International Applications)

**ATTORNEY'S DOCKET NUMBER**  
 MUHLEN ET AL-1 PCT

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**METHOD FOR GASIFYING ORGANIC MATERIALS AND MIXTURES OF MATERIALS**

the specification of which (check only one item below):

- [ ] is attached hereto.  
 [ ] was filed as United States application

Serial No. \_\_\_\_\_

on \_\_\_\_\_

and was amended

on \_\_\_\_\_ (if applicable).

- [ X ] was filed as PCT international application

Number \_\_\_\_\_ PCT/EP00/09275

on \_\_\_\_\_ 22 SEPTEMBER 2000

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

**PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:**

| COUNTRY<br>(if PCT, indicate "PCT") | APPLICATION NUMBER | DATE OF FILING<br>(day, month, year) | PRIORITY CLAIMED<br>UNDER 35 U.S.C. 119 |
|-------------------------------------|--------------------|--------------------------------------|---|
| GERMANY                             | 199 45 771.9       | 24 SEPTEMBER 1999                    | [ X ] YES [ ] NO                        |
|                                     |                    |                                      | [ ] YES [ ] NO                          |
|                                     |                    |                                      | [ ] YES [ ] NO                          |
|                                     |                    |                                      | [ ] YES [ ] NO                          |
|                                     |                    |                                      | [ ] YES [ ] NO                          |

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|---|--|--|--|---|
| I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.   |  |  |  |   |
| (Application Number)  |  | (Filing Date)  |  |   |
| I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application: |  |  |  |   |
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| U.S. APPLICATIONS   |  | STATUS (Check One)   |  |   |
| U.S. APPLICATION NUMBER   | U.S. FILING DATE                                   | PATENTED   | PENDING                                    | ABANDONED   |
|   |  |  |  |   |
| PCT APPLICATIONS DESIGNATING THE U.S.   |  |  |  |   |
| PCT APPLICATION NO.   | PCT FILING DATE                                    | U.S. SERIAL NUMBERS ASSIGNED (if any)                                    |  |   |
|   |  |  |  |   |
| <p><b>POWER OF ATTORNEY:</b> As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration numbers).</p> <p>KURT KELMAN, Registration No. 18,628<br/>         ALLISON C. COLLARD, Registration No. 22,532;<br/>         EDWARD R. FREEDMAN, Registration No. 26,048;<br/>         ELIZABETH COLLARD RICHTER, Registration No. 35,103</p> <p>FREDERICK J. DORCHAK, Registration No. 29,298<br/>         WILLIAM C. COLLARD, Registration No. 38,411<br/>         ROBERT W. GRIFFITH, Registration No. 48,956</p>                       |  |  |  |   |
| Send Correspondence to:   |  | COLLARD & ROE, P.C.<br>1077 Northern Boulevard<br>Roslyn, New York 11576 | Customer No. <u>25889</u>                  | Direct Telephone Calls to:<br>(name and telephone number)<br>(516) 365-9802 |
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| I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.   |  |  |  |   |
| SIGNATURE OF INVENTOR 201<br><u>X</u> <u>A. Mühlen</u>  |  | SIGNATURE OF INVENTOR 202<br><u>X</u> <u>C. Schmid</u>                   |  |   |
| DATE <u>21 March 2002</u>   |  | DATE <u>21 March 2002</u>  |  |   |